Senior Thesis

AN X-RAY DIFFRACTION STUDY OF TWO CONCRETIONS FROM THE OHIO SHALE

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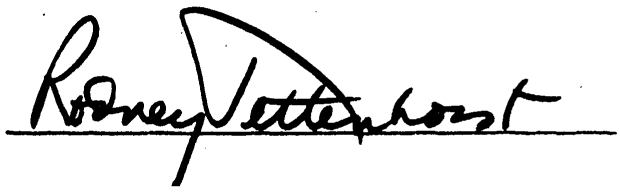
Advisor: 

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Introduction

Concretions are secondary structures occurring in sedimentary rocks. Generally, these structures are spherically shaped and are composed of concentrations of minerals in concentric layers around a nucleus. Commonly sandstones, mudstones, and shales contain concretionary structures.

Geologists for years have theorized on the possible origins of concretions. Even today with more research being done, no one is absolutely sure what conditions were present and necessary to form these structures. Many studies hypothesize that decay of organic matter in sediments sets up a chemical imbalance in a localized volume, which allows the precipitaion of minerals in concentric layers around a nucleus.

Concretions occur in the Olentangy and Ohio Shales which outcrop in the central Ohio area. Two concretions were collected from the Ohio Shale and analysed for mineral composition using X-ray diffraction. Shale samples were also collected and analysed by the same method.

Stratigraphy

The Ohio Shale is an Upper Devonian black shale which outcrops throughout Ohio and into northern Kentucky. It lies along a shale belt approximately 300 miles wide and extends from southern New York to northern Texas. The shales have different formational names depending on the locality,

but all are stratagraphically equivalent. In central Ohio, the Ohio Shale outcrops along river and stream banks, and in road cuts. The thickness of the shale averages 600 feet. It is underlain conformably by the Middle Devonian Olentangy Shale, and overlain conformably by the Mississippian Bedford Shale.

Two theories of origin for the late Devonian shales are given by Baxtrom (1968). The "deep-water" theory proposes that the shale sediments were transported from the Acadian Orogeny, which lies to the east, and deposited in the western part of the Appalachian geosyncline. The "shallow-water" theory is based upon a transgressive sea which reworks soils by wave action, and deposits the sediments in the slighly deeper waters just under storm wave base. Anaerobic conditions prevail in both theories thus organic matter was preserved giving the shales their black color. Baxtroms analysis of the Ohio Shale favors the "shallow-water" theory.

Carbonate Concretions in the Ohio Shale

Concretions found in the Ohio Shale occur in the lower sixty feet of the formation. These concretions are composed of carbonates and sulfides, and are described by Clifton (1957) and Barth (1975). Also, barite nodules have been noted by Holden (1979) in the Cleveland Shale in Cuyahoga County, Ohio. The Cleveland Shale is considered a member of the Ohio Shale.

Early mention of concretions in the Ohio Shale was made by N. H. Winchell (1874). Stauffer (1911) provided a better description of the concretions. He referred to them as "iron-stones." Bedding planes can be seen in some of the spheroids and often the nuclei are crystalline masses of calcite or barite. Fossils have also been found, also fish bones and pieces of wood at the centers. Stauffer believed that concretions are epigenetic, or secondary, because of the arching of the shale around them, and their compositional uniformity.

Clifton (1957) reviewed previous theories as well as more modern ones. Newberry (1873) theorized that the concretionary masses formed in place in soft mud. As the sediments compacted, the hard spheroids resisted compaction and the shale layers tended to bend around the body. The compaction may have caused the spheres to become more spheroidal. Later general theories, dealing with bedding around concretions, place the time of development after initial compaction. Westgate (1926) used this idea to formulate a theory based on the flow of groundwater just above the impervious Olentangy Shale. The mineralized water would deposit minerals at a specific site thus forming a concretion.

Still later theories are based on a syngenetic origin because an epigenetic origin would cause shale distortions laterally, and these distortions have never been documented.

Barth (1975), gave a specific theory on the origin of Ohio Shale concretions. He made three assumptions: 1) concretion growth occurred during a time when the muds were still plastic, and growth and deposition were concurrent, 2) further growth only occurred while circulation of water solutions went from sea bottom to the concretion site, 3) the starting nucleus was usually organic. The theory holds that different bacteria groups processed the organic material and precipitated iron compounds, carbonates, and sulfides depending upon the chemical composition of the water medium surrounding the concretion. This mechanism allows the concretions to be composed of different mineralic layers, which is actually the case.

Collection Site Location and Description

The shale samples and two concretions were collected from the lower sixty feet of the Ohio Shale. The outcrop is located in the City of Worthington in Franklin County approximately one-quarter mile west of the I-270, U.S. 23 interchange on the south side of I-270 (Figure 1). The site is an ephemeral waterfall face cut into the Ohio Shale. The waterfall has only recently formed, and is the result of a channel which carries runoff from parking lots to the Olentangy River. The falls (Plate 1) are on a steep embankment with relief of five meters. The embankment used to be a river bank before the river was moved for construction

Figure 1

Location of outcrop site shown by square.

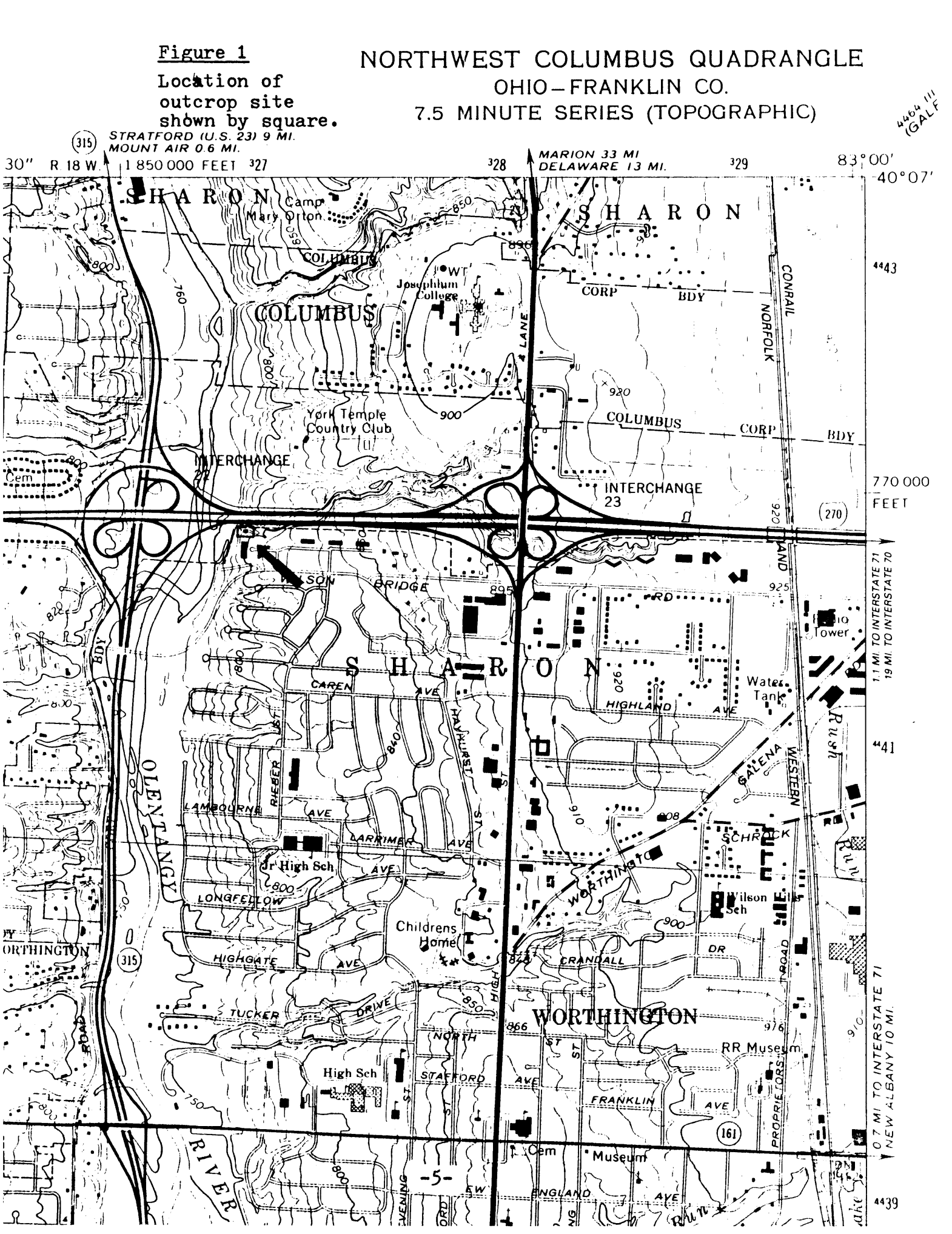


Plate 1 Waterfall cut face in the Ohio Shale. Note the concretion in the upper right-hand corner and also the green shale.

of a freeway. An example of the rapid erosion taking place is found in the upper left-hand corner of Plate 1. The concrete mass is the base of a fence post which was placed into the ground less than fifteen years ago. It is now two meters in air above the surface of the stream bed.

Lithologic Section and Hand-specimen Description

The outcrop section is approximately three meters high (Figure 2). The lower portion of the section is the black Ohio Shale. Just one meter above, there are two green shale beds separated by a thin black shale bed. Above the two green shales, 1.5 meters of black shales are present. At the top, a thin layer of glacial till covers the Ohio Shale.

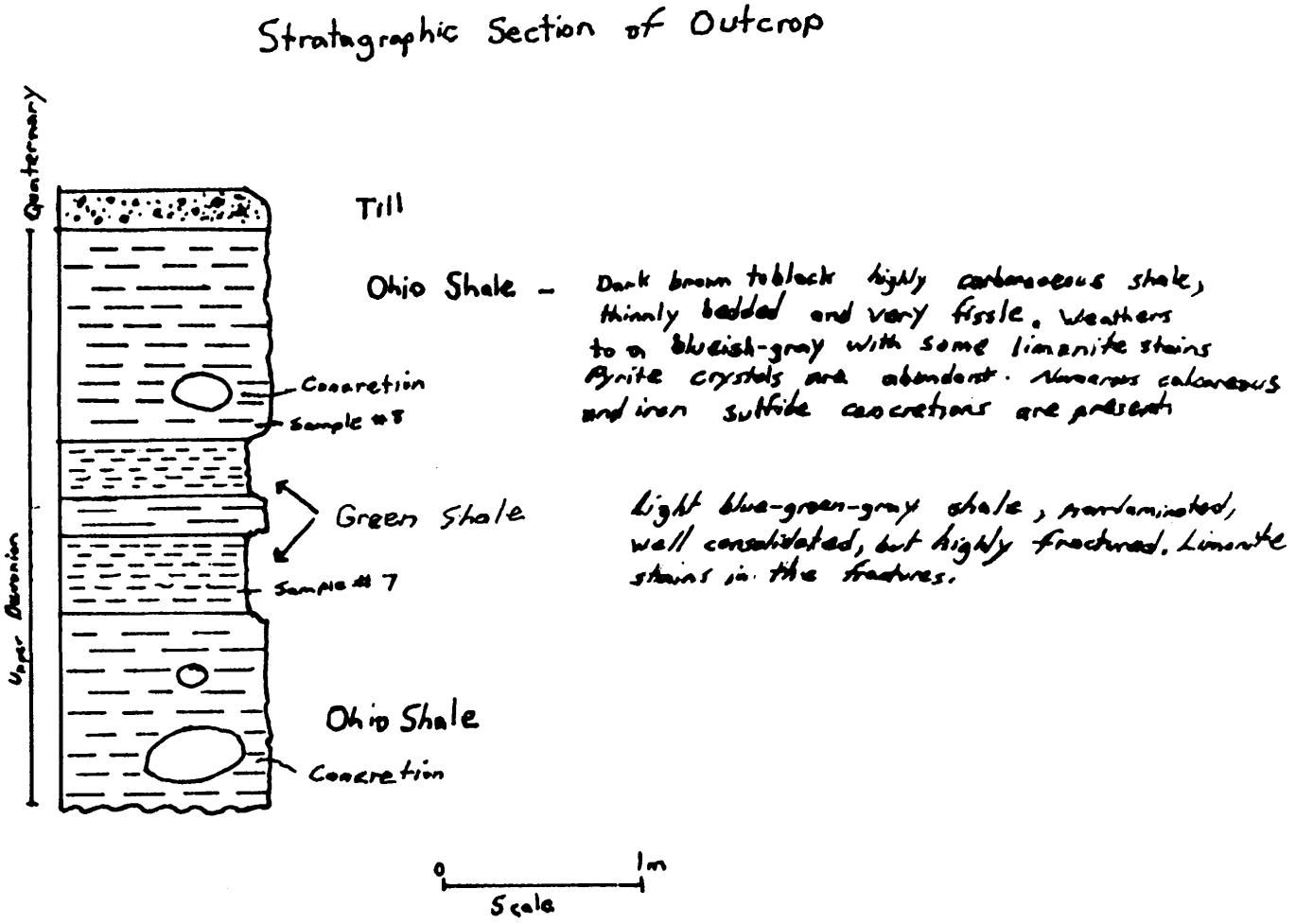
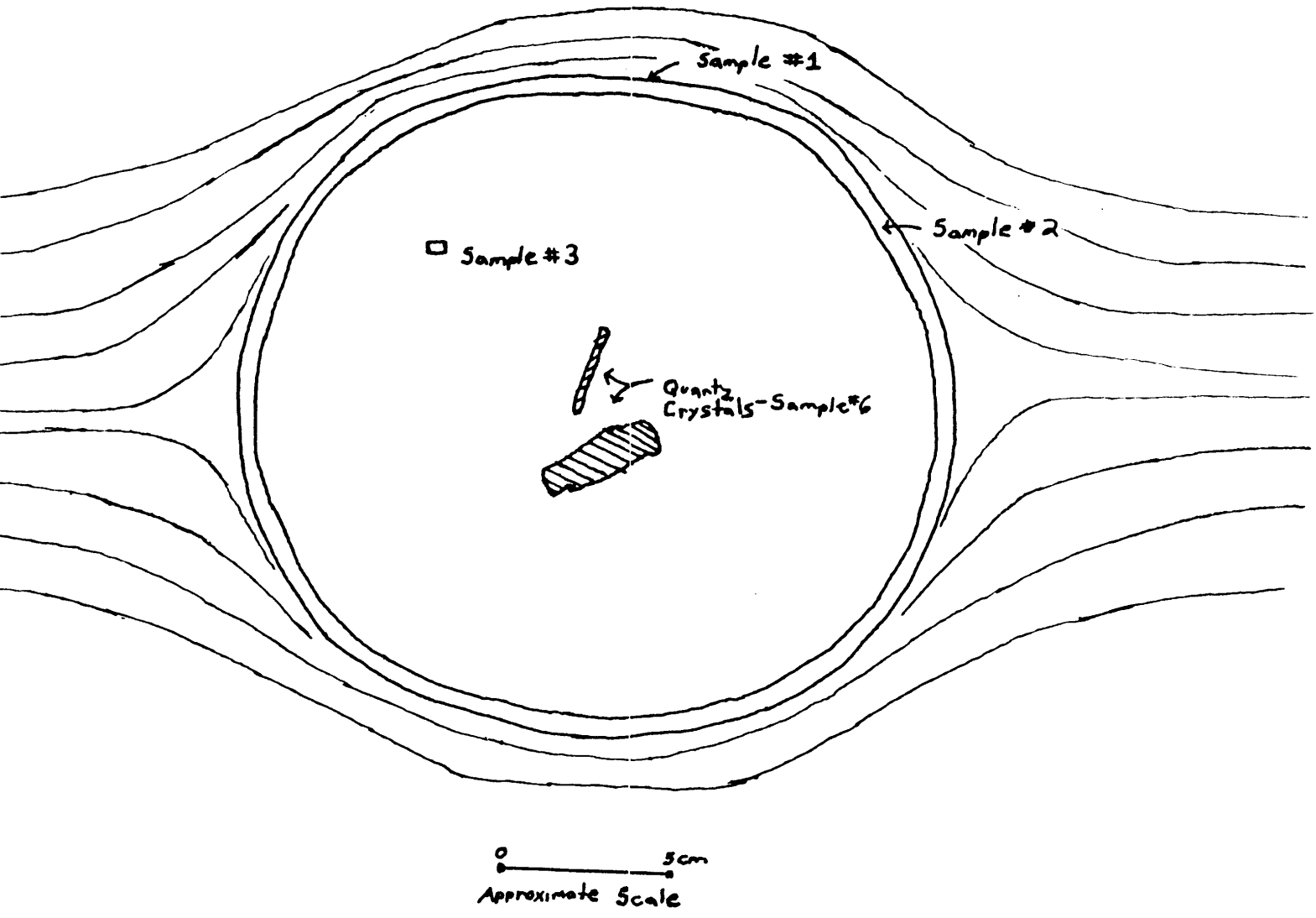


Figure 2

The green shale beds are described as minor interbeds of gray and blue-gray mudstone by Schwietering (1970). These beds are located in the lower part of the Ohio Shale. Thus the existance of the beds provides correlation that the concretions were found in the lower sixty feet of the Ohio Shale. The larger concretion A was found above the green shales, and the smaller concretion B was found below the green shales.

The concretions were very soft and wet when collected. Each had the consistency of a fine mud. They were taken indoors and air-dried for over a month. Once the water evaporated, they became very lightweight and friable.



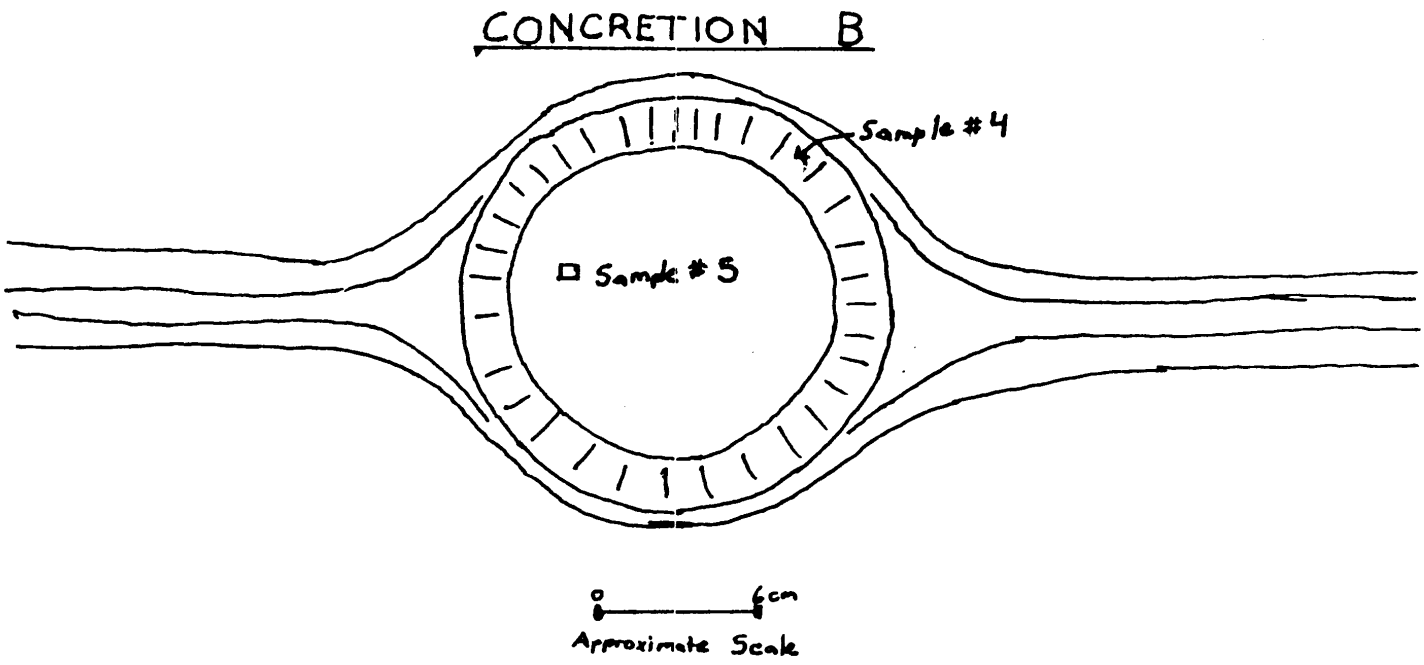


Figure 3 Diagrams of the two concretions.

Plate 2

Plate 3

2 & 3 - Close-up views of concretion A.

A total of eight samples were taken from the shales and concretions (Figures 2 & 3). Sample #1 was taken from the outer layer of concretion A, and appears as a brown platey layer which crumbles very easily. Sample #2 was taken immediately below sample #1. This layer was a light yellow-brown and was very powdery when dry. This layer can also be seen in Plates 2 & 3 as the light yellow band around the outside of the concretion. Sample #3 is from the interior of concretion A. It was a deeper orange-brown color than sample #2 and had the same textural qualities. Sample #4 was taken from concretion B. The outer layer was charcoal-gray and powdery like the two previous samples. When wet, this layer had metallic-looking bands in a radial pattern around the concretion. When dry, these bands could not be seen. Sample #5 is from the interior of concretion B. It consisted of a gray-brown powder very similar to samples #2 and #3. Sample #6 (Figure 4) was a piece of one of the crystals that was found in the interior of concretion A. The crystals were very lightweight and porous. Thin crystal blades are found in the interior of the hollow crystal forms. Sample #7 was a piece of the green shale and sample #8 was a piece of the black shale.

X-ray Diffraction Analysis Procedures

Each of the samples was ground in a mortar and pestle into a very fine silt size powder. Part of each powder

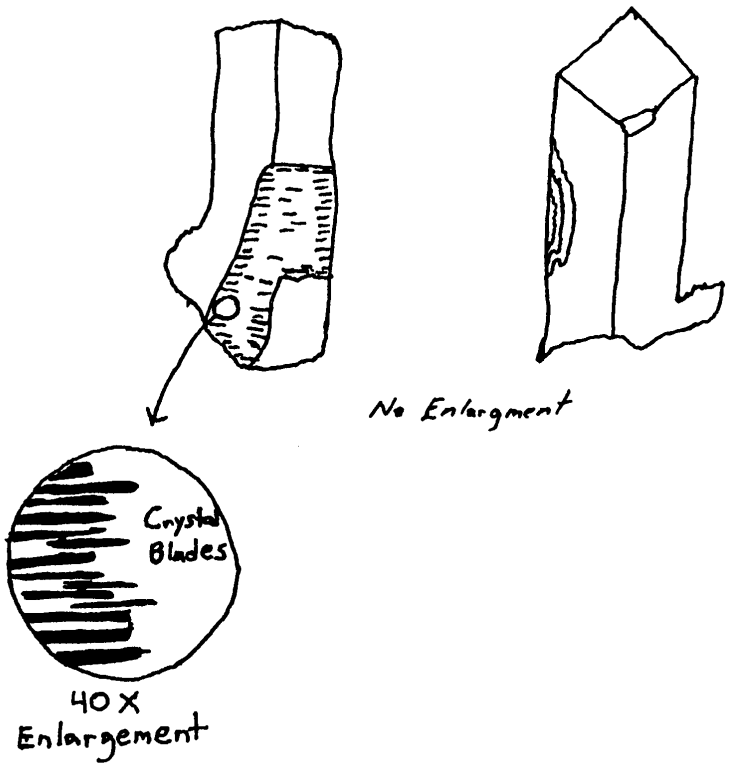


Figure 4 Quartz crystals found in concretion A.

sample was then mixed with distilled water and allowed to settle for approximately one minute. A clay-sized fraction was then drawn with an eye dropper off the top of the mixture. The dropper fluid was then placed on a clean glass slide and air dried. Once dry, the slide was placed in an ethylene glycol chamber for over 24 hours to allow the clays (if present) to absorb the ethylene glycol and expand. This expansion allows the X-ray diffractometer to register their existence. The remaining dry powder of each sample was placed in a dry powder slide. The slide was filled and leveled off.

Mineral analysis was accomplished by X-ray diffraction analysis using Philips XRG-3100 equipment. Settings on the equipment included 35 kilovolts, 15 miliamps,

500 counts/second range, scintillation detector, scanning speed was $2^{o}/2\theta$ min, and the X-ray chart speed was 60 inches/ hr. A theta compensating slit along with a graphite monochromater was used.

A total of sixteen diffraction patterns were produced; two for each sample. The dry powder sample ran from 4^{o} to 56^{o} and the sample of the clay-size fraction ran from 2^{o} to 30^{o}. Copies of the eight dry powder patterns are shown at the end of this paper. The clay-size fraction patterns are not shown because they produced no new findings different from the dry powder samples.

Results

All three samples taken from concretion A showed the same three mineral constituents: quartz, goethite, and ferrihydrite. The quartz peaks were the strongest and sharpest. The goethite peaks were less well defined, and the ferrihydrite peak was small and broad. Peak sharpness gives an approximate indication of the degree of crystallinity. A sharper peak indicates better crystallinity.

The pattern for sample #4 shows a big change in composition from the previous samples. All the peaks are very sharp. The largest ones are pyrite, and smaller ones quartz. The occurence of pyrite explains the metallic-looking bands seen in this layer when concretion B was wet. The pattern for sample #5 is similar to those of #1-3.

The goethite peaks are slightly sharper, in the pattern of sample #5, but 10 Å clay peaks and plagioclase feldspar peaks are also present, and are not seen in #1-3.

Perhaps the most interesting pattern is provided by sample #6. The crystals, even though very light and porous, were very difficult to grind. They are composed primarily of quartz. However, an unexpected mineral, whewellite, which is a calcium oxalate whose chemical formula is $CaC_2O_4 \cdot H_2O$, is also present. Whewellite is a fairly rare mineral and will be discussed in detail.

Samples #7 and #8 were of the two shales. These two samples were fairly similar. Both contained quartz, 10 Å clays, and plagioclase feldspar. However, sample #8, the black Ohio Shale, contained a 7 Å clay (kaolinite or chlorite) and pyrite. These two mineral differences may account for the color differences between the two shales.

Occurence of Goethite and Whewellite

Goethite is a common secondary mineral and is usually formed under oxidizing conditions as a weathering product of iron-bearing minerals. The goethite in the concretion had a very fine granular form which was uniform throughout both concretions, with the exception of sample #1. This uniformity may may suggest a homogeneous iron content before alteration.

Whewellite is a relatively rare mineral found in hydrothermal veins and in sedimentary secondary structures.

Whewellite crystals tend to be colorless with a hardness of 2½, and have been found in carbonate concretions in marine shales. The first report of whewellite in North America came from a concretion in the Bearpaw Shale of Late Cretacious near Havre, Montana (Pecora, 1954). A second similar find is documented from the Ohio Shale (Hyde, 1966). Carbonate concretions were collected from the lower 60 feet of the Ohio Shale near Cleveland. Upon breaking open these concretions, numerous crystals of different minerals were found including large pure whewellite crystals.

Whewellite was found only in concretion A along with the quartz crystals. After careful optical examinations, both macroscopically and microscopically, no whewellite crystals could be seen. An orange anomalous iron coating on the crystals prevented optical identification of the crystals.

A Possible Origin of the Goethite Concretions

The origin of the iron to form the goethite is somewhat puzzling. The Ohio Shale does contain considerable amounts of iron carbonates and iron sulfides. However, since concretion B contained unweathered pyrite, it would seem that the source of the iron was not the pyrite. The presence of whewellite may provide the key to the source of the iron.

Leavens (1968) gives a formula for the precipitation of whewellite under anaerobic conditions:

$$CaCO_3 + CO_2(aq) + 2H^+ + 2e^- = CaC_2O_4 \cdot H_2O$$

Under the same conditions that break down water, native iron can also be precipitated (Leveans, 1968).

Therefore it may be that decay of an organic body in the soft Ohio Shale sedimants set up a chemical imbalance which allowed the precipitation of quartz, native iron, and whewellite simultaneously. The quartz and iron grew together and might have caused the unusual appearence of the quartz crystals (Figure 4).

Once the chemical imbalance was removed through total decay of organic matter or the supply of iron was cut off, the native iron would be subject to alteration. As the shale reached the surface through geologic processes, weathering completely altered the native iron to goethite, thus leaving only the quartz and whewellite as evidence of the origin of the former concretion.

Conclusions

The goethite concretions are probably somewhat common in the Ohio Shale. A search through the literature provided no previous documentation of this type of concretion. Even though they may be common, the time span that they may be seen in an outcrop is very short. The unconsolidated nature of them allows rapid erosion, thereby leaving no trace.

X-ray diffraction provided identification of the mineralogical make-up of the concretions. Goethite, quartz, and clays were primary constituents. A very unexpected find was whewellite. However, the presence of whewellite provided a necessary clue to suggest a possible origin of the concretions.

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